Fuel Quality Assurance Research and Development and Impurity Testing in Support of Codes and Standards

SCS007

Team:

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Overview

Timeline and Budget

- Project start date: 10/1/06
- Project end date : 9/30/22

Barriers

- G. Insufficient Technical Data to Revise Standards
- K. No Consistent Codification Plan and Process for Synchronization of R&D and Code Development

Budget

- Total project funding: $6,375K
  - Hydrogen Fuel Quality Standards and Hydrogen Safety Sensor : $3575K (2006-2015)
  - Hydrogen Contaminant Detector (HCD) $2,800K (2013 - Present)

FY20 HCD Funding : $500K

Partners/Collaborators

- **H2Frontier (Burbank, CA)**
- **SKYRE (Formerly Sustainable Innovations)**
- **NREL, Bill Buttner**
- **VI Controls, Neal Pedersen (Los Alamos)**
- **ONEH2 (H2F Affiliate, testing partner)**

Outline

- **Project Background: Scope and Approach**
- **HCD Development and Deployment**
  - **Offline HCD Deployment Status**
    - **Field Testing at H2 Frontier filling station**
    - **HCD Validation and Verification Testing at NREL**
    - **Preliminary H_2S Results**
    - **Technology Transfer Activity: SKYRE**
  - **Inline HCD Development**
    - **Motivation/Relevance: TPP and PBI-based Analyzers**
    - **TPP Findings**
    - **PBI Results**
- **Summary/Future Work**

Project Background

Relevance

- Device needed to detect impurities ≥ SAE J2719 levels in **t < 5min**.
- Offline & Inline HCD Development

Approach 1 (Offline Analysis):
Field test HCD at HRS, have independent validation and work with manufacturer on commercialization plan

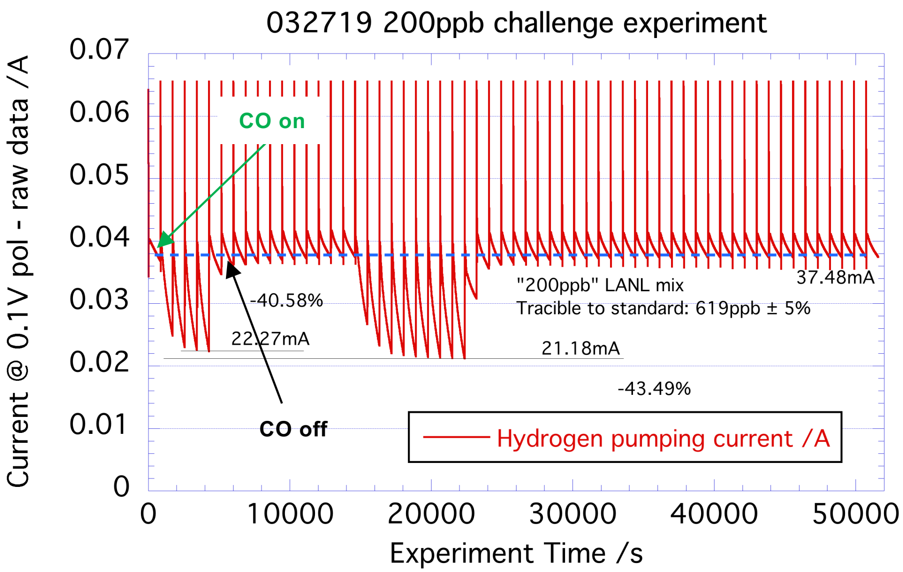
Approach 2 (Inline Analysis):
Replace Nafion® with a proton-conducting membrane that will not require water to function.

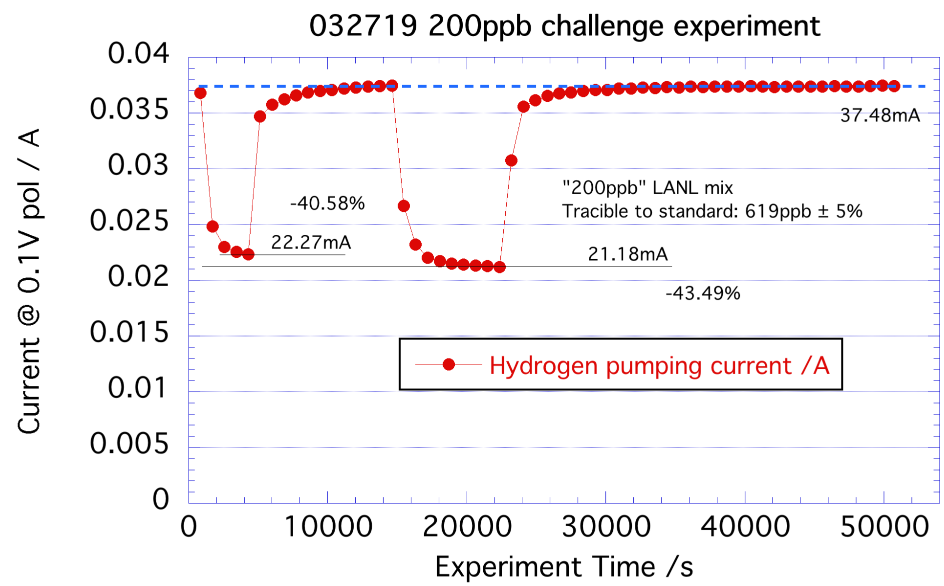
Impact
Successful implementation provides an inexpensive method to detect fuel impurities ≥ the SAE levels, possibly protecting FC fleets.

HCD Field Results : SAE/ISO CO Level

Offline Analysis

- Certified 200ppb bottles of CO/H_2 mixtures are <u>not commercially available.</u>
- A low pressure bottle (<25psi) of test gas was prepared using a NIST traceable standard.
- Raw data(left) plot shows measured current value (0.1V polarization) with clean-up voltage (1.5V) and without on the right.





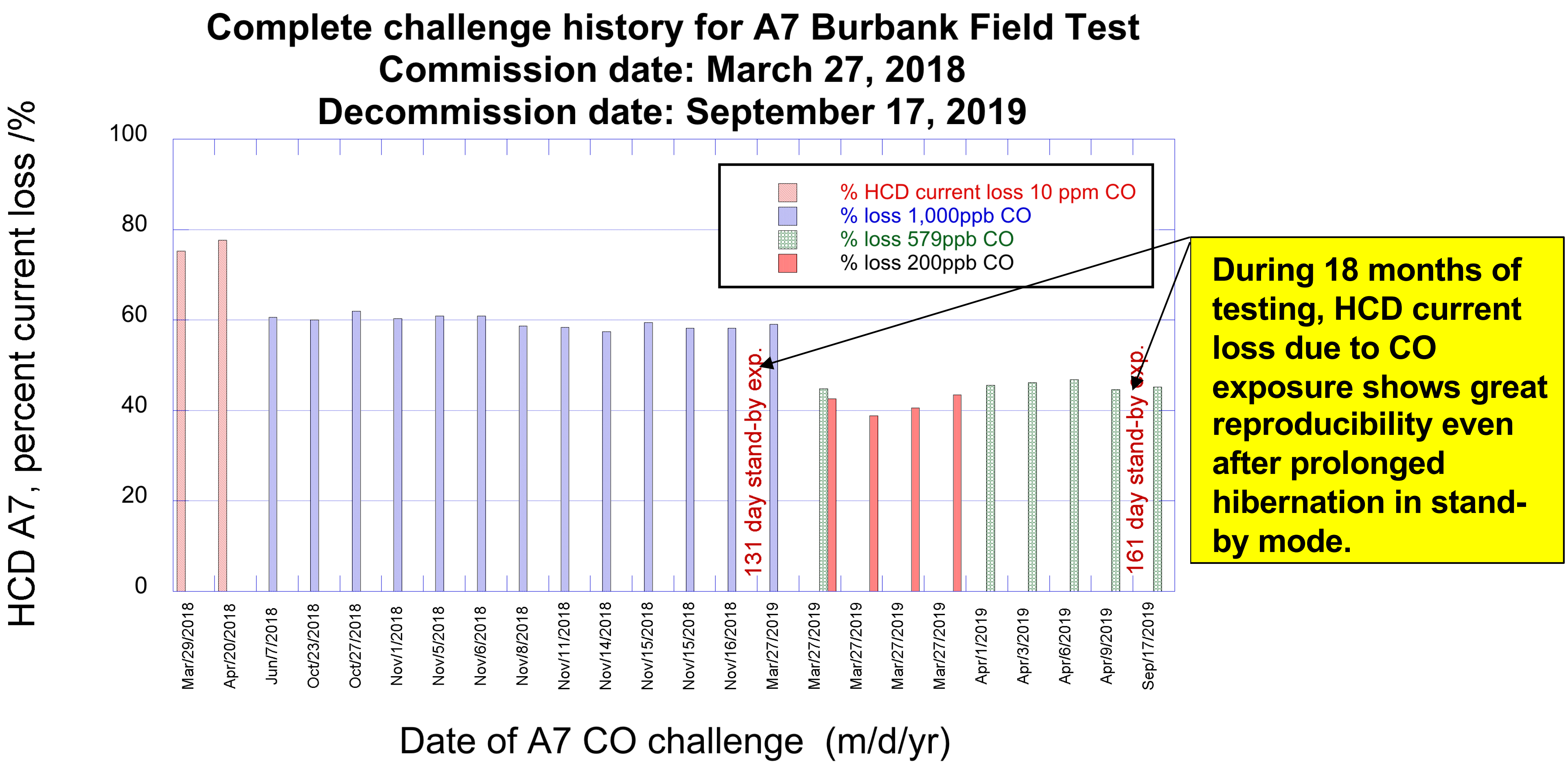
- HCD successfully detected 200ppb CO outside of laboratory conditions.
- A large current loss is observed when 200ppb CO is injected into the H2F hydrogen stream.

Accomplishment

HCD Field Results : Long Term Stability

Offline Analysis

- Recall: Except for Start-up of the station reformer, a real-time, **CO poisoning event was not experienced during field testing at H2F**. Periodically, the HCD test stream was switched to a bottle of H_2 containing a certified conc. level of CO contamination.
- Challenge Tests performed at H2F:



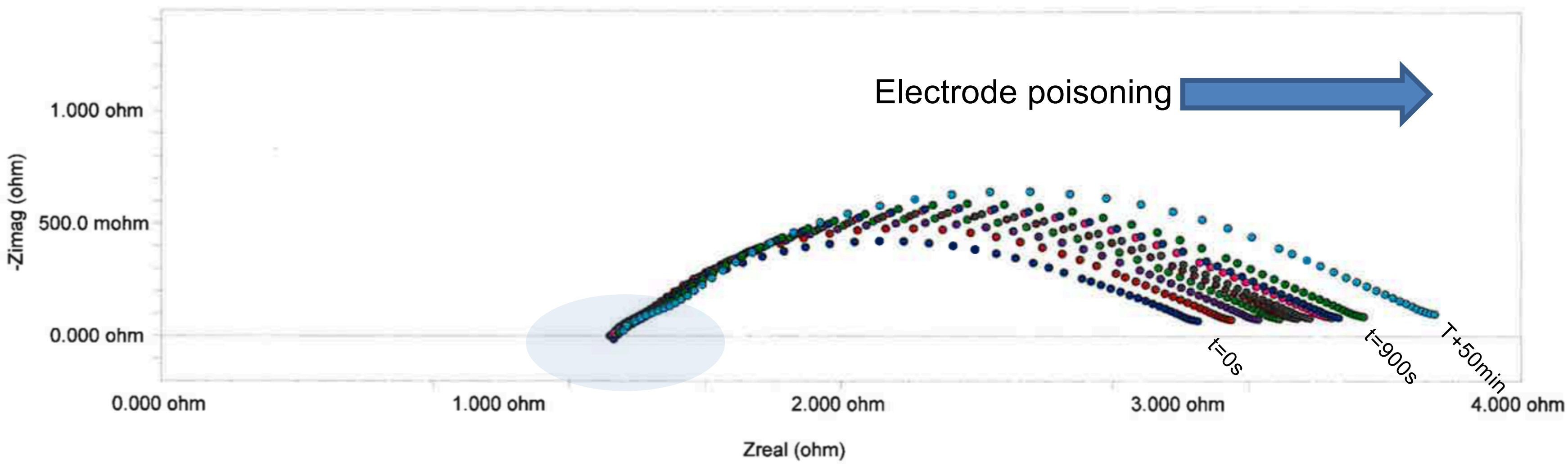
Accomplishment

Initial H_2S Results

Milestone : March 2020

Offline Analysis

- EIS performed sequentially WITHOUT clean-up pulses
- Data for 9.6ppb H_2S cumulative exposure test
- Initial impedance spectra show an increase in CTR, indicative of catalyst poisoning
- More testing with ISO/SAE limit of 4ppb H_2S is scheduled.



Reviewer's Comment:
The team has spent too much time focusing on CO, even though CO can be seen as a canary species.

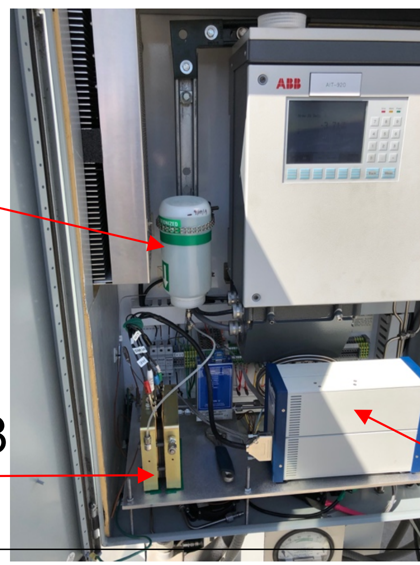
Accomplishment

LANL/NREL visit to H2F

Offline Analysis

- Purpose of visit to Burbank H2F station:
  - Collect final testing data for HCD A7 device.
  - Service zero-gas and span gas bottles.
  - Install new expanded volume, passive water delivery system for humidification.
  - Replace T controller.
- NREL Technical staff met LANL staff at the H2F station to monitor field test experiments/operations and to see first-hand, sampling options and manner of insertion of LANL HCD into the H2F production systems.
- Install new HCD (interdigitated flow field) for Field Testing at H2F.

DI water to supply internal humidification system.



LANL HCD A8

Gamry Potentiostat

Reviewer's Comments:
The **presentation did not get into detail regarding how well coordinated the partnerships and collaborations might be**, although the collaboration on DOE Small Business Innovation Research (SBIR) and SBV proposals for the technology commercialization partner is noteworthy.

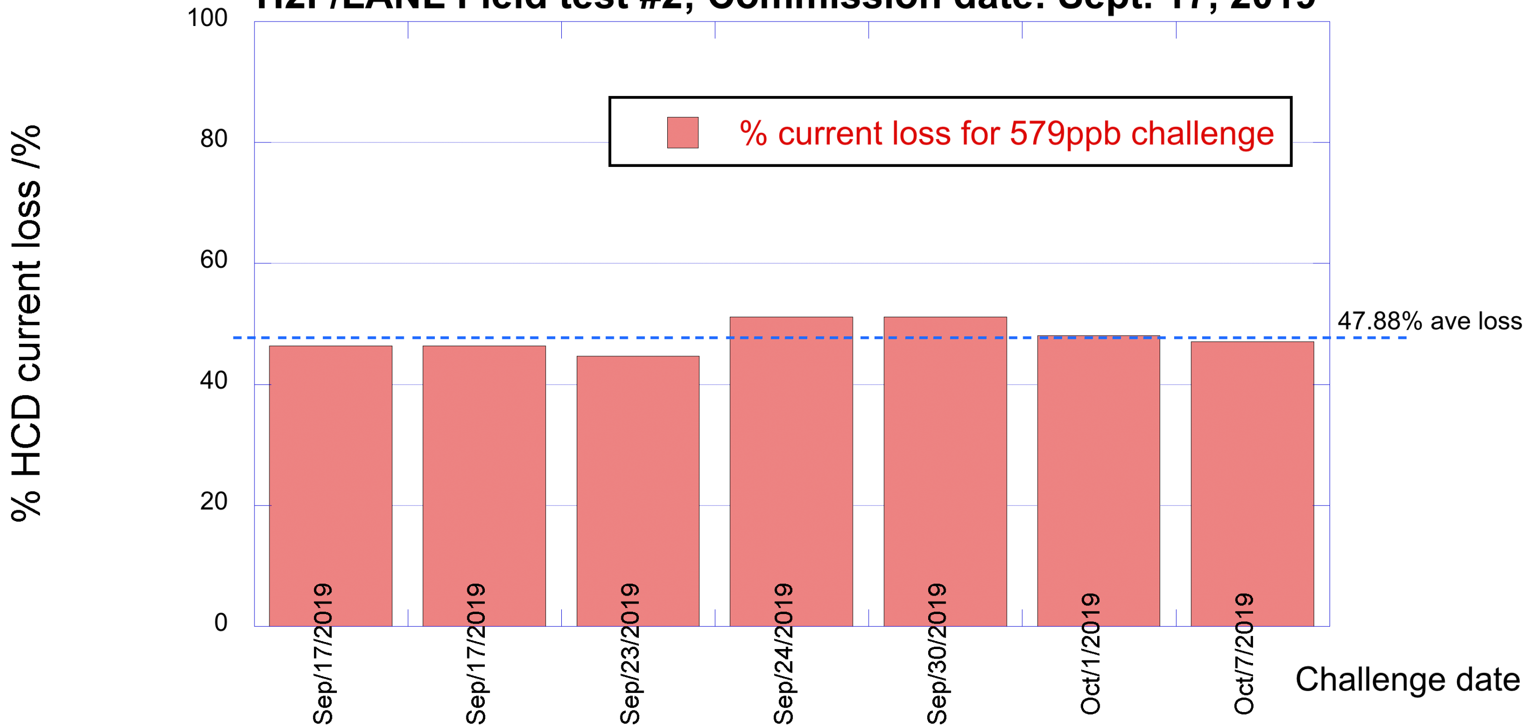
Collaboration and Coordination

LANL/NREL at H2F: New HCD with Interdigitated Flow Field

Offline Analysis

- A new interdigitated flow field at the working electrode configuration was installed at H2F
- Test for advantages in sensitivity, response time, etc.

A8_1 Challenge history conducted at H2Frontier, Burbank CA
A8_1 Nafion® based, interdigtated electrode / expanded H2O reservoir system
H2F/LANL Field test #2; Commission date: Sept. 17, 2019



Reproducibility of the LANL HCD approach in field conditions is excellent.

Accomplishment

Preparation for NREL to Perform Validation and Verification Testing

Offline Analysis

- LANL Mission Move Agreement prepared in order to loan NREL LANL's HCD and Gamry 600+ Reference Potentiostat.
- A sampling / switching system and flow control modules permanently transferred to NREL.
- LANL and NREL technical staff worked together for 2 days to review start-up, and operation of LANL HCD technology.

Photo provided by NREL Hydrogen Systems Engineer Mathew.

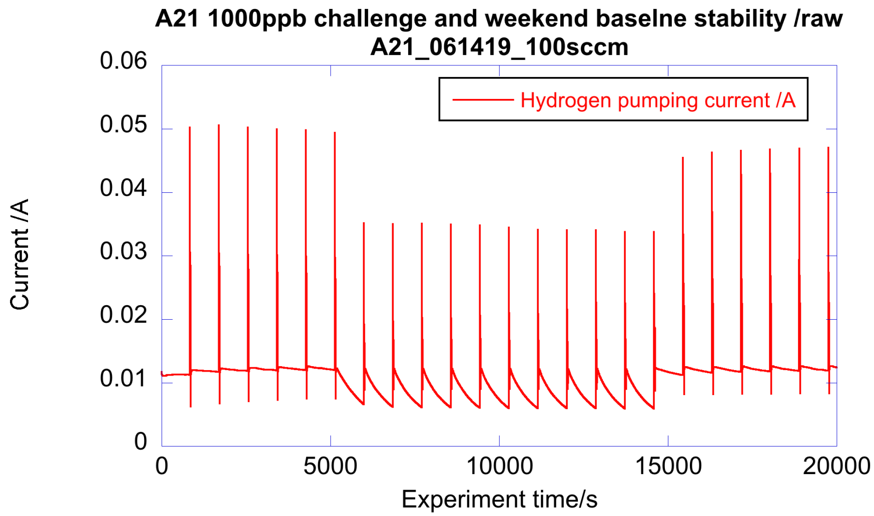
<u>LANL Test set-up successfully integrated at NREL</u>

LANL HCD to be tested along side the only other contamination technology: a commercial FTIR-based analyzer system.

Collaboration and Coordination

HCD Validation Results

Offline Analysis

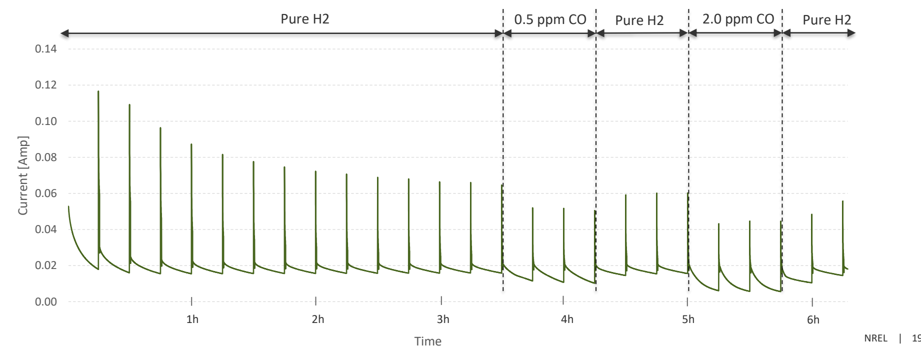


LANL Results prior to sending to NREL

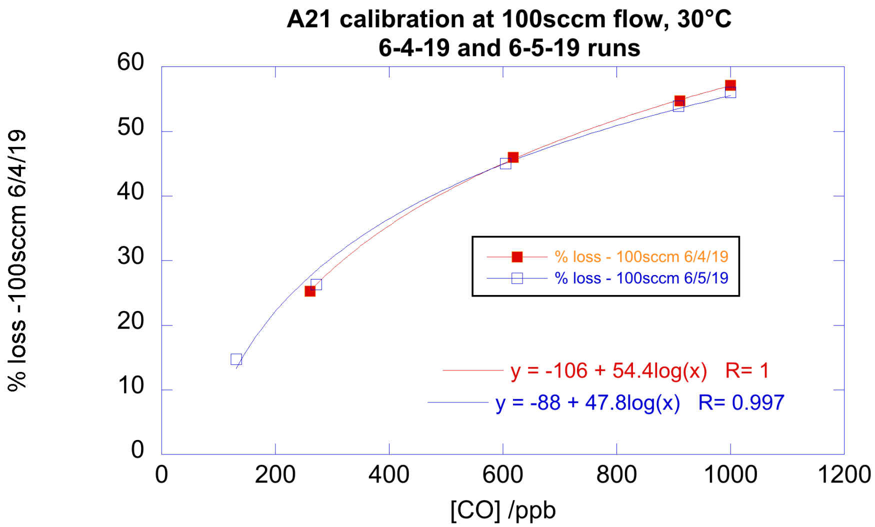
Electrochemical Sensor Response
(Preliminary Test)

A cycle consists of 3 steps:

- Conditioning at 1.5V for 600 seconds Start
- Delay 20 seconds
- Continuous Pulsed-Chronoamperometric Operation at 0.1V for 830 seconds with periodic 30 sec 1.5 V pulses



Initial Validation and Verification Testing at NREL



- V&V testing began in December 2019.
- Identical operating modes
- Using the Calibration Chart allows data to be compared although different [CO] were tested.

Results obtained at respective facilities closely agree

Accomplishment

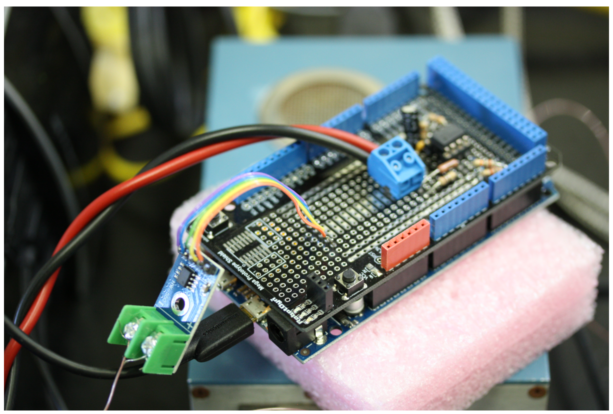
HCD Technology Transfer
LANL to SKYRE

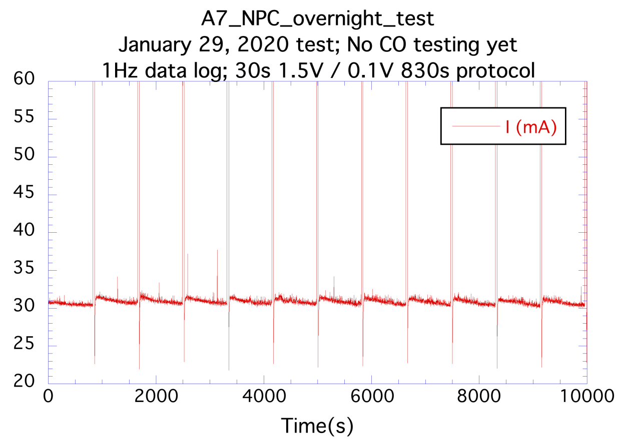
Offline Analysis

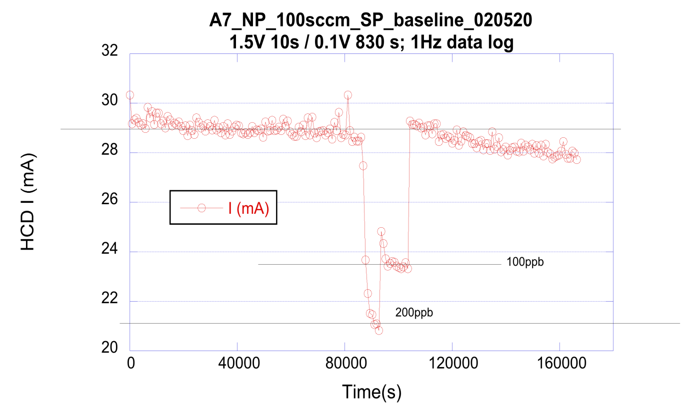
Collaboration and Coordination

Develop low cost Hardware	Develop low cost Electronics	Evaluate new LANL HCD devices	
3/30/2020	**6/30/2020**	**9/30/2020**	**12/30/2020**

Accomplishment: Developed Gen 1 Electronics







- New control module based on Arduino architecture **< $50**
- Gen 1 Electronics **developed and tested**
- 1st CO **response at/below** ISO / SAE fuel qual. spec.

Successful Technology Commercialization Fund (TCF) project underway (Jan – Dec of 2020)

Approach 2 (Inline): HCD based on PBI or TPP

Inline Analysis

Relevance:

Develop a HCD that functions like the technology shown today <u>without need for water or oxygen</u>. Reduce system complexity and cost and potential to operate ***inline*** at the nozzle.

Approach:

2 viable options (developmental stage):

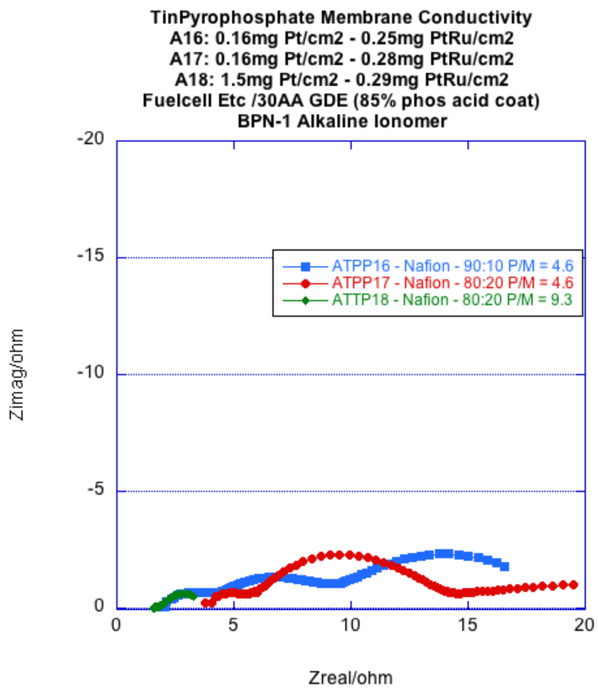
- Tin Pyrophosphate (TPP) based electrolyte
- PBI based electrolyte

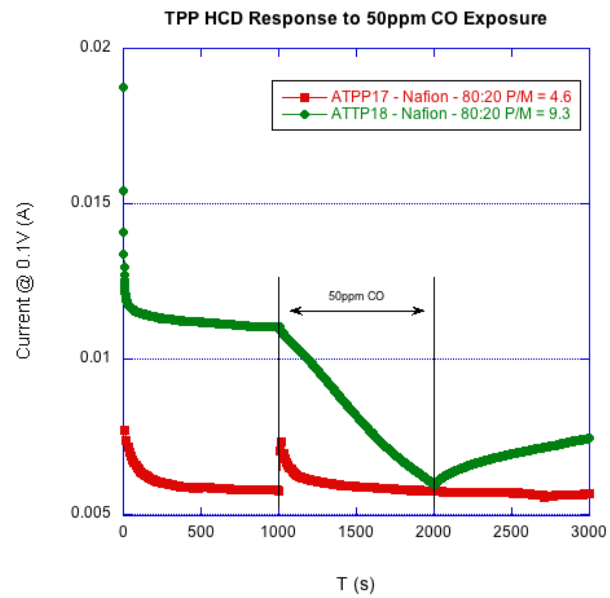
PBI membranes prepared by LANL researchers

TPP-based HCD

Inline Analysis

Analyzer TPP	Loading (2.275 cm2 area)	TPP Membrane Nafion	GDE/GDL - H3PO4	BPN-1 Alk. Ionomer Sensor Electrode	Baseline Current	100 PPM CO Current	50 PPM CO Current
ATPP16	0.16 mg Pt/cm2 - 0.25 mg PtRu/cm2	90:10 P/M = 4.6	FC etc/30AA - 15M	0.13 mg total dry	2.9 mA	no response	no response
ATPP17	0.16 mg Pt/cm2 - 0.28 mg PtRu/cm2	80:20 P/M = 4.6	FC etc/30AA - 15M	0.13 mg total dry	5.7 mA	no response	no reponse
ATPP18	1.5 mg Pt/cm2 - 0.29 mg PtRu/cm2	80:20 P/M = 9.3	FC etc/30AA - 15M	1.0 mg total dry	Bline	27.86 mA (Bline) 18.63 mA (CO)	11.02 mA (Bline) 6.0 mA (CO)





ATTP16
Baseline I = 2.9mA @ 0.1V
No CO Response

- Varied ratio of TPP content and increased P/Sn ratio to improve conductivity.
- Only one HCD responded to CO at concentrations > 250X
- Baseline Performance was unstable
- **Annual milestone met (No Go Decision)**

Reviewer's Comment:
It is also unclear whether TPP is viable.

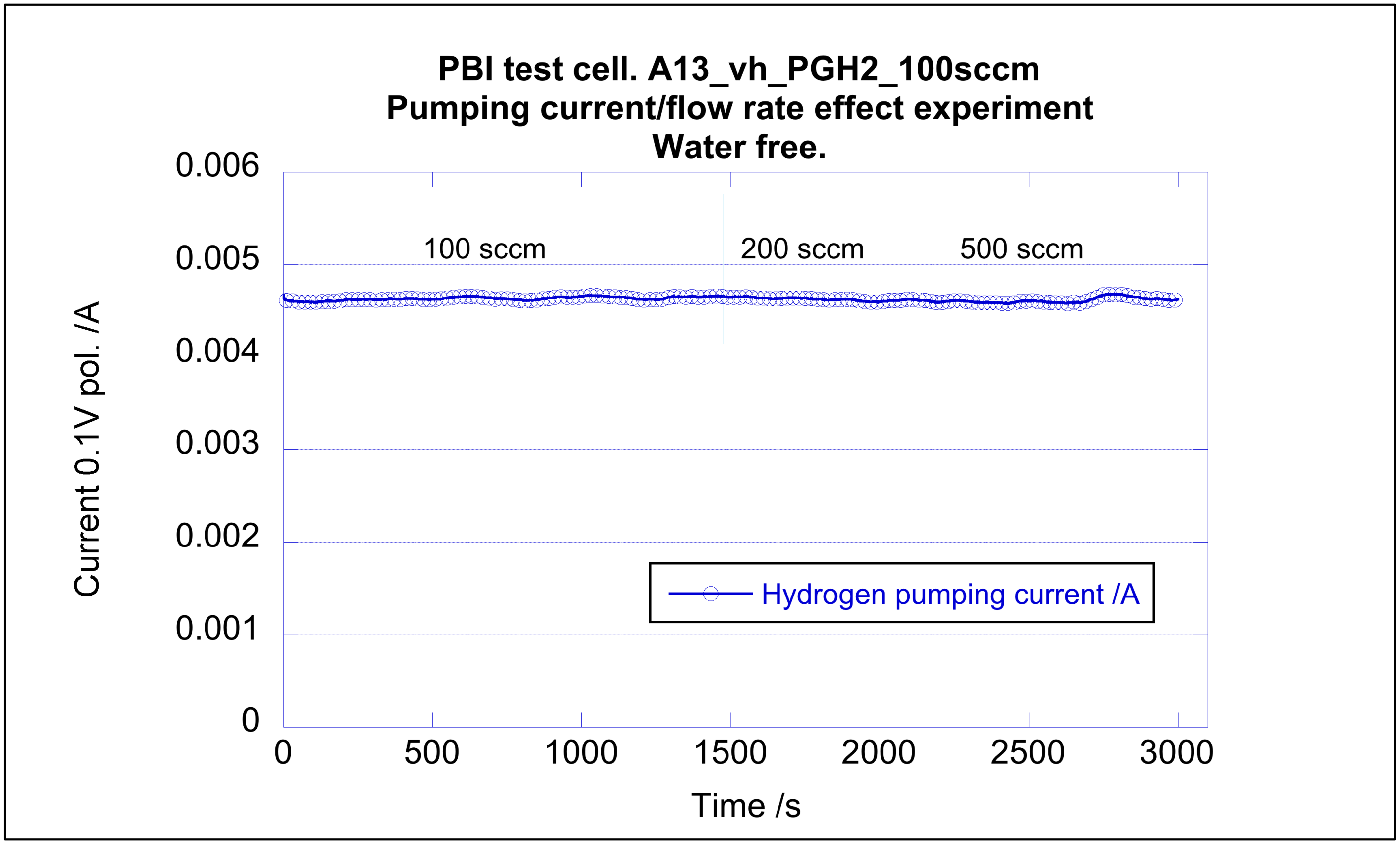
Accomplishment

Down Select PBI over TPP for HCD

Inline Analysis

Milestone : June 2019

Data presented at last AMR

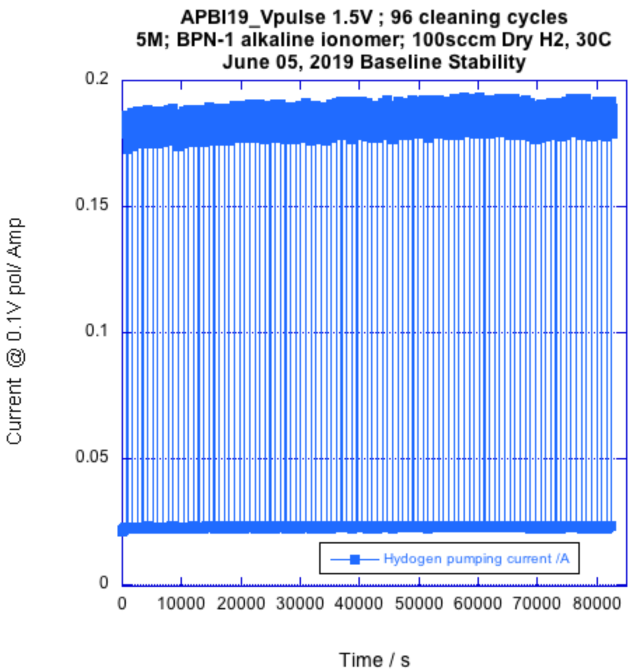


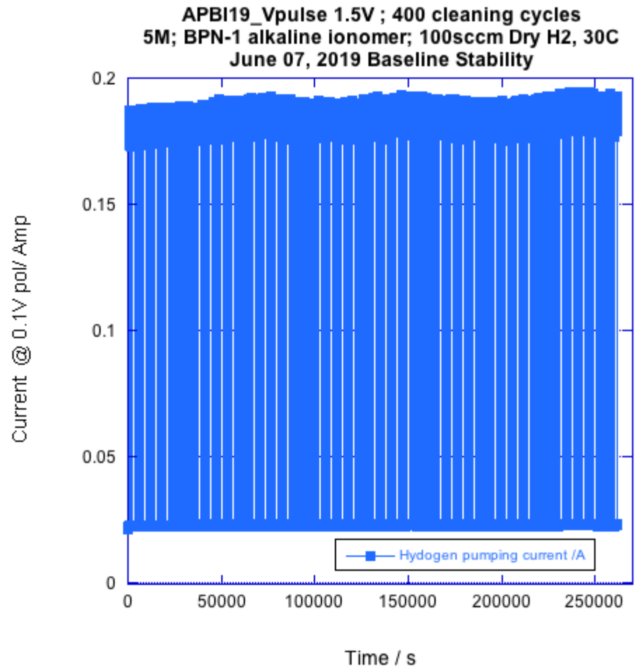
PBI-based HCD operated in completely water-free, dry H_2 stream. The current response remained constant even after a 5X increase in flowrate. Short term testing < 1hr.

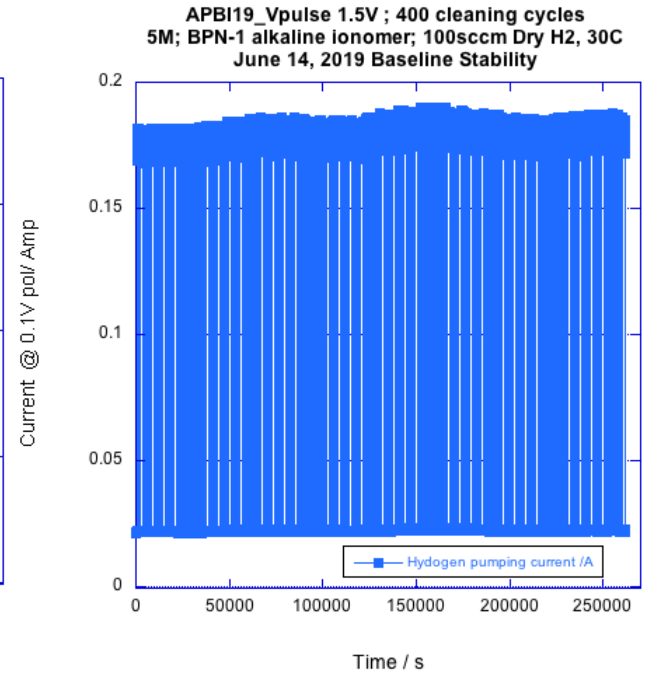
Baseline stability: PBI membrane

Inline Analysis

Milestone : Sept 2019







- PBI membrane prepared with 5M H_3PO4, excess applied to GDE/GDL
- Identical Proposed Operating Mode

PBI based HCD maintained baseline current within +/-5% when exposed to dry neat hydrogen at 30C for 1 week. **(Annual milestone met)**

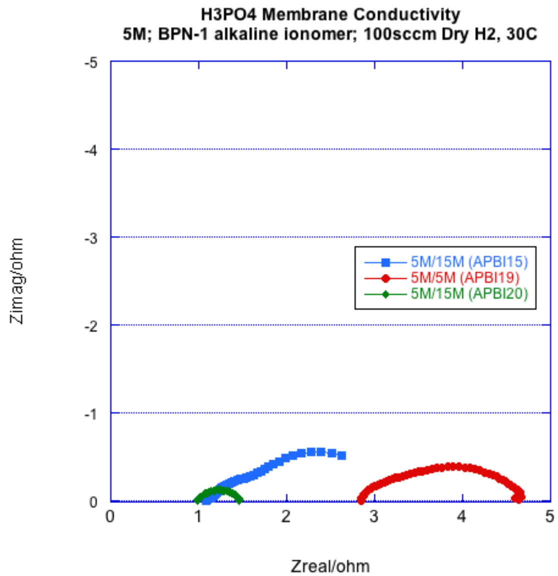
Accomplishment

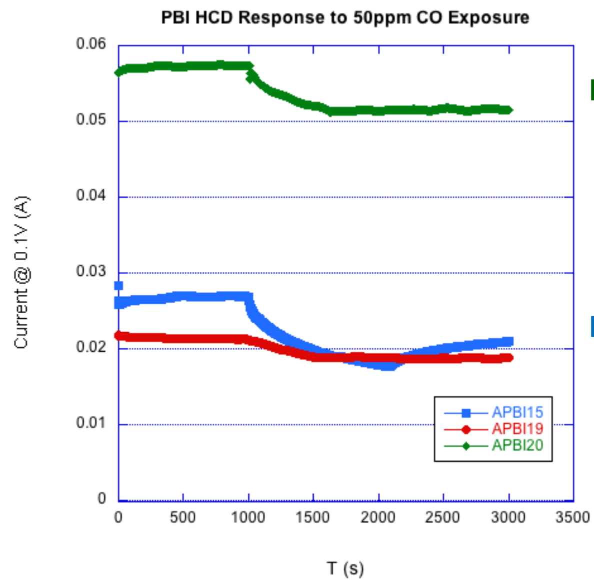
PBI HCD Results

Milestone : Dec 2019

Inline Analysis

Analyzer PBI	Loading (2.275 cm2 area)	H3PO4 Membrane	GDE/GDL - H3PO4	BPN-1 Alk. Ionomer Sensor Electrode	Baseline Current	50 PPM CO Current	10 PPM CO Current	1 PPM CO Current
APBI15	1.5 mg Pt/cm2 - 0.2mg PtRu/cm2	5M	FC etc/30AA- 15M	0.98 mg total dry	26.66 mA	17.74 mA	n/a	25.37 mA
APBI19	0.15 mg Pt/cm2 - 0.2mg PtRu/cm2	5M	FC etc/30AA - 5M	0.13 mg total dry	21.22 mA	18.92 mA	no response	no response
APBI20	0.35 mg Pt/cm2 - 0.36mg PtRu/cm2	5M	FC etc/30AA - 15M	0.3 mg total dry	57.33 mA	51.38 mA	no response	n/a





- Tunable features:
  - Increasing H_3PO_4 reduces HFR, and improves baseline currents.
  - Decreasing Ionomer in electrode, decreases electrode resistance, and improves baseline currents.
- Responds to higher CO concentrations, our focus is now on improving sensitivity.

Accomplishment

Summary

HCD Development and Deployment:

Offline Analysis:

- Nafion® based HCD developed with a patented wicking system
- HCD tested in the field
  - Sensitive to SAE J2719 levels of CO (200ppb)
  - Stable baseline over extended periods
  - Calibration maintained over a year of testing
- HCD delivered to NREL for testing
  - Independent validation
- TCF/SKYRE
  - GEN 1 Electronics have been tested
  - HCD with GEN 1 electronics were able to detect 100 ppb CO

Inline Analysis:

- Assembly of TPP composite membranes with GDEs to measure conductivity and HCD performance completed. (No Go)
- PBI membranes can function in a HCD (Down-selected)
  - Eliminates the need for water wicking system. Provides ability to operate inline and under pressure
  - Varying Electrode Ionomer, H_3PO_4, and Pt loading is a tunable feature

Proposed Future Work

- **HCD Development and Deployment**

<u>Offline HCD Deployment Status</u>

- Field testing to take place at Sysco Foods Distribution Facility in Riverside, CA
- Work on integrating HCD and GEN 1 electronics/hardware into a package
- Deliver validated Triad HCD devices to SKYRE
- Work collaboratively with SKYRE to develop a commercialization pathway
- Continue H_2S experiments at SAE/ISO levels

<u>Inline HCD Development</u>

- Optimize tunable properties to improve sensitivity to CO and continue work with H_2S at SAE/ISO levels.
- Report on the response of PBI-membrane based analyzer to different concentrations of H_2S and identify cleaning protocol to return analyzer to baseline.
- Install a PBI-membrane based analyzer at the H2Frontier fueling station and obtain a stable baseline (current level within $\pm$10%) for > 10 days.
- Quantify CO and H_2S response of analyzer: Design an HCD capable of detecting both CO and H_2S at or below SAE J2719 levels (200ppb for CO and 4 ppb for H_2S).

Any proposed future work is subject to change based on funding levels.

Response to Reviewer’s Comments

Reviewer’s Comment:
It is also unclear whether TPP is viable.
LANL: Team down selected to PBI-based Inline HCD development.

Reviewer’s Comment:
The team has spent too much time focusing on CO, even though CO can be seen as a canary species.
LANL: Efforts are now including H_2S detection

Reviewer’s Comments:
The presentation did not get into detail regarding how well coordinated the partnerships and collaborations might be, although the collaboration on DOE Small Business Innovation Research (SBIR) and SBV proposals for the technology commercialization partner is noteworthy.
LANL: Successful collaborations with NREL, H2F, SKYRE and VI Control Systems are explained in detail throughout presentation.

Acknowledgements

LANL staff would like to thank:

- DOE-EERE Fuel Cell Technologies Office
  - Laura Hill: Technology Development Manager
- Codes & Standards Tech Team
- The Audience…